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DOI:

[10.1016/j.fuel.2013.11.053](https://doi.org/10.1016/j.fuel.2013.11.053)

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Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Blissett, R, Smalley, N & Rowson, N 2014, 'An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content', *Fuel*, vol. 119, pp. 236-239.

<https://doi.org/10.1016/j.fuel.2013.11.053>

[Link to publication on Research at Birmingham portal](#)

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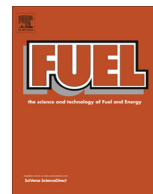
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Short communication

An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content[☆]R.S. Blissett^{a,*}, N. Smalley^b, N.A. Rowson^a^a School of Chemical Engineering, University of Birmingham, Edgbaston B15 2TT, United Kingdom^b RockTron International Limited, Wessex House, Pixash Lane, Keynsham BS31 1TP, United Kingdom

ARTICLE INFO

Article history:

Received 31 October 2013

Received in revised form 21 November 2013

Accepted 25 November 2013

Available online 5 December 2013

Keywords:

Rare earth elements

Coal fly ash

Utilisation

ABSTRACT

Rare earth elements have been identified by the European Commission as a critical raw material. Six European coal fly ashes have been investigated for their rare earth element content. A coal fly ash from the UK has levels of rare earth element that are approaching that which might be commercially viable to exploit. After classification there was found to be a slight enrichment in the smaller non-magnetic inorganic content of the coal fly ash.

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1. Introduction

In 2010 the Raw Materials Supply Group of the European Commission published a report highlighting a group of materials that were to be defined as critical: a raw material is defined critical “when the risks of supply shortage and their impacts on the economy are higher compared with most of the other raw materials” [1]. Forty-one raw materials were analysed with respect to the politico-economic stability of the producing country, their geographical concentration, their substitution potential, and their rate of recycling. As a result of this analysis a list of 14 raw materials were defined critical at an European Union level. Rare earth elements (REY) (15 lanthanides plus yttrium and scandium) were included on this list. REY use is expected to increase over the next decade, and it is expected to do so in many clean technology areas [2]. In order to maintain Europe’s competitive standing in these areas, alternative sources to conventional mining deposits of these materials may need to be considered.

Hard coal fly ashes (CFAs) have been estimated to contain 445 ppm REY on an average global basis [3]. There have been many reports of CFAs with REY contents that far exceed the world average (circa 0.1–1.0 wt%): elevated REY levels have been reported in

the Russian Far East coal deposits [4–6]; Western Siberia, Russia [7]; the Daqingshan and Jungar coalfields, Inner Mongolia [8–11]; the Heshan and Fusui coalfields of southern China [12,13]; the Songzo coalfield, southwestern China [14]; eastern Yunnan, China [15]; and the Fire Clay coal bed in Eastern Kentucky, United States [16,17]. For a review of coal deposits as a potential source of REY, readers are referred to the work of Seredin and Dai [18].

Although some work has been done on analysing utility combustion CFAs (see for example: [9,17]), a large proportion of the reported elevated levels of REY come from exploratory coal samples that have been laboratory ashed for analysis. This is extremely useful for identifying coal resources that might be exploited for a dual energy REY extraction purpose, but it does not address the large amount of CFA currently being produced, or that already in landfill. A recent study examined a variety of CFAs that are collected from different rows of the electrostatic precipitators in various power plants [19]; total REY content ranged from 187 to 600 ppm. Two Bulgarian CFAs and four Turkish CFAs analysed as part of that study were found to have REY content in the range 209–230 ppm.

In 2009 Europe produced 35 Mt of CFA [20]. A larger selection of European CFA samples must be analysed in order to assess the potential for it to be considered as a REY resource. To this end a preliminary screening study of six CFAs, three from the UK, and three from Poland was undertaken. The most promising CFA was then selected and subjected to both a size classification and a more comprehensive separation process to assess whether the REY is concentrated in particular size and/or mineralogical fractions.

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2. Experimental

Six different CFAs were obtained via the CFA processing company RockTron International Ltd. Hereafter, they will be referred to as UK-1, UK-2, UK-3, P-1, P-2 and, P-3: the Polish ashes are derived from bituminous coal; UK-2 and UK-3 from a bituminous coal/biomass blend; and UK-1 is from a semi-anthracitic coal source. One of the samples was further sieved into six size fractions. In addition to the CFA samples, also provided were samples from various points in RockTron's CFA processing pilot plant (for further details see [21]). The source of each CFA is shown in Table 1. For trace element analysis, a prepared sample of CFA (0.2 g) is added to lithium borate flux (0.9 g), mixed well, and fused in a furnace at 1000 °C. The resulting melt is then cooled and dissolved in 100 mL of 4% HNO₃/2% HCl solution. This solution is then analysed by inductively coupled plasma-mass spectrometry (ICP-MS).

3. Results and discussion

Geochemically, REY distribution can be classified into three groups: the total REY can be split into light (LREY – La, Ce, Pr, Nd, and Sm), medium (MREY – Eu, Gd, Tb, Dy, and Y), and heavy (HREY – Ho, Er, Tm, Yb, and Lu) groups. Yttrium, although not a lanthanide, possesses an ionic radius similar to Ho and so is often shown on REY distribution plots between Dy and Ho. Seredin and Dai [18], following analysis by the Industrial Minerals Company of Australia (IMCOA), devised a new classification which bears more relation to the likely supply and demand forecast over the next few years. This is also a threefold classification: it is made up of critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu) groups. This classification makes an assessment of the distribution more relevant to the requirements of industry.

Table 1 summarises the ICP-MS results. All of the CFAs analysed had favourable distributions in terms of their critical element content. With a critical content of greater than 30%, and an outlook coefficient (critical/excessive) of greater than 0.7, the CFAs would

be termed as *Group II-promising* using Seredin and Dai's criteria [18]. Counter to this is the fact that none of the CFAs had total rare earth oxide (REO) content over 600 ppm. Seredin and Dai [18] also discuss the relevant cut-off grade for REO from the combustion products of coal. This is given as 800–900 ppm for coal seams more than 5 m in thickness. However, all of the samples analysed currently are already being produced on an industrial basis. There is no mining or exploration cost associated with them. Further work is required to assess the ease of extraction of the current samples but it is conceivable that on this basis the cut-off grade might be reduced.

All of the CFAs show a broadly similar REY distribution as evidenced by Fig. 1. UK-1 CFA had the highest total REO content of the samples analysed at 579 ppm. It has a pronounced Eu maximum and is classified as M-type, subtype 2; this distribution is typical of certain hydrothermal REY ores and of certain alkali mafic

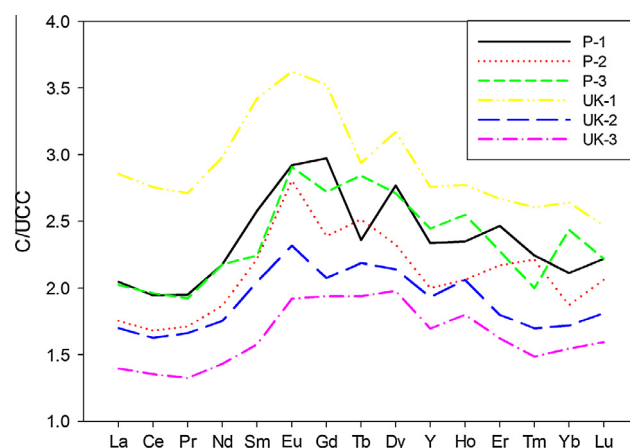


Fig. 1. M-type rare earth elemental distribution normalised to data for the upper continental crust [22] for six European CFAs.

Table 1
REY content of six industrial CFAs (ppm).

Element	P-1	P-2	P-3	UK-1	UK-2	UK-3
La	61.4	52.6	60.7	85.7	51.0	41.9
Ce	124.5	107.5	125.5	176.5	104.0	86.6
Pr	13.9	12.2	13.7	19.3	11.8	9.4
Nd	56.6	48.6	56.6	77.6	45.6	37.2
Sm	11.6	10.0	10.1	15.4	9.2	7.1
Eu	2.6	2.5	2.6	3.2	2.0	1.7
Gd	11.3	9.1	10.4	13.4	7.9	7.4
Tb	1.5	1.6	1.8	1.9	1.4	1.2
Dy	9.7	8.1	9.5	11.1	7.5	6.9
Y	51.4	44.0	53.8	60.7	42.5	37.3
Ho	1.9	1.7	2.0	2.2	1.7	1.4
Er	5.7	5.0	5.2	6.1	4.1	3.7
Tm	0.7	0.7	0.7	0.9	0.6	0.5
Yb	4.7	4.1	5.4	5.8	3.8	3.4
Lu	0.7	0.7	0.7	0.8	0.6	0.5
ΣREY	358	308	359	481	294	246
LREY (%)	74.8	74.9	74.3	77.9	75.5	74.0
MREY (%)	21.4	21.2	21.8	18.8	20.9	22.1
HREY (%)	3.8	3.9	3.9	3.3	3.6	3.9
Critical	127	110	130	161	103	88
Uncritical	98	84	95	134	80	66
Excessive	133	115	134	186	111	92
Outlook	0.96	0.96	0.96	0.86	0.93	0.95
Critical (%)	35.6	35.6	36.1	33.4	35.1	35.8
ΣREO	431	371	432	579	354	297
LOI @ 950 °C	4.0	6.6	8.9	14.8	10.7	12.0

Table 2
REY content of size classified UK-1 CFA (ppm).

Element	$d < 38 \mu\text{m}$	$38 \geq d \geq 63 \mu\text{m}$	$63 \geq d \geq 90 \mu\text{m}$	$90 \geq d \geq 125 \mu\text{m}$	$125 \geq d \geq 150 \mu\text{m}$	$d < 150 \mu\text{m}$
La	99.3	68.5	57.2	54.3	50.2	56.0
Ce	207.0	142.5	114.0	107.0	102.5	108.0
Pr	24.2	16.5	13.4	12.6	12.0	13.2
Nd	93.4	63.1	50.3	48.1	48.7	49.5
Sm	17.6	12.2	8.7	9.1	8.9	10.3
Eu	3.8	2.7	2.0	2.0	1.8	2.0
Gd	15.9	10.3	8.6	7.8	7.4	8.8
Tb	2.3	1.5	1.2	1.1	1.0	1.3
Dy	13.5	9.3	7.1	7.4	7.2	7.4
Y	74.6	46.6	37.1	38.1	35.5	40.7
Ho	2.6	1.6	1.4	1.5	1.3	1.4
Er	7.1	4.9	3.8	3.9	3.6	4.2
Tm	1.2	0.7	0.6	0.6	0.5	0.7
Yb	6.4	4.5	3.6	3.4	3.7	3.6
Lu	1.0	0.6	0.5	0.6	0.5	0.5
ΣREY	570	385	309	297	285	307
LREY (%)	77.5	78.6	78.7	77.7	78.1	77.1
MREY (%)	19.3	18.2	18.1	19.0	18.6	19.6
HREY (%)	3.2	3.2	3.2	3.3	3.4	3.4
Critical	195	128	101	101	98	105
Uncritical	157	107	88	84	79	88
Excessive	218	150	120	113	108	114
Outlook	0.89	0.85	0.84	0.89	0.90	0.92
Critical (%)	34.2	33.2	32.8	33.8	34.3	34.2
ΣREO	686	464	372	358	343	370
LOI @ 900 °C	8.2	14.2	20.1	36.4	31.7	31.6

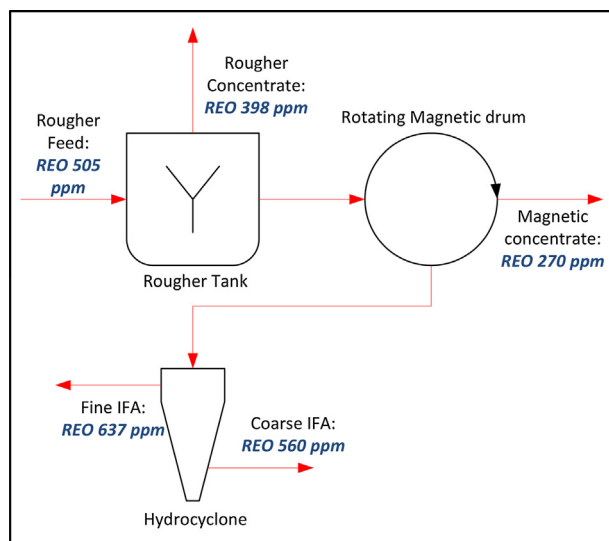


Fig. 2. The REE appears to be concentrated in the non-magnetic inorganic matter of UK-1 ash according to the samples taken at various places in the processing scheme.

volcanic ashes [15], although it has also been ascribed to the higher sorption of MREY in humic matter relative to LREY and HREY [18].

In another recent paper on the subject, Hower et al. [19] summarised data on REY content of size classified CFA from Dai et al. [9]. They report a similar trend to that observed in Table 2: namely, an increase in total REO content as the particle size decreases. As their study was the only one known to have reported such data, they were unable to ascertain whether this finding is consistent with other CFAs. The current study provides further data to support this suggested trend. It is also evident, that on a percentage basis, there appears to be a minimum of critical REY content, as well as a maximum of LREY content, between 63 and 90 μm . This is in contrast to the trend observed in Hower et al. [19] which shows the critical REY content with a maximum between 48 and 96 μm .

Interest has grown in recent years in the concept of multi-component utilisation of CFA [21,23]. Within this concept it is envisaged that CFA, an intrinsically heterogeneous product, can be separated into distinct components. Fig. 2 illustrates a processing scheme capable of separating a raw CFA feed into four components: (1) an organic concentrate, (2) a magnetic concentrate, (3) a coarse improved residual fly ash (IFA), and (4) a fine IFA. It can be calculated from Fig. 2 that, relative to the feed CFA, the REO content is reduced by 47% and 21% in the magnetic concentrate and organic concentrate, respectively. Conversely, the REO content increases by 11% and 26% in the coarse and fine IFA, respectively. This result is in accordance with the size fraction analysis but it also suggests that a large proportion of the REY in CFA is present in the non-magnetic inorganic material. Recent research has shown [24], using Ce as a proxy for all the lanthanides, that REY elements reside homogeneously within the glass phase. This has implications for REY extraction as it requires that the leaching agents must contact the entire particle. A possible explanation for why the REY appears to be more concentrated in the smaller size fractions is that, as both Table 2 and previous studies show [25], larger size fractions of CFA tend to have a higher carbon content. The relatively modest reduction in REY content in the organic concentrate might be masked in this instance by the fact that the sample is taken from only the first stage in a multi-stage froth flotation circuit. It is evident from Table 3 that the organic content of the flotation concentrate is just 50.8%. As such, a sample taken at this point will have a higher fine CFA content than the concentrate from a stage further down the froth flotation circuit. This analysis shows that it is possible to enrich CFA through a multi-stage processing route to levels approaching that required for economic extraction. If the carbon concentrate is re-burned in the power plant [21], and the magnetic concentrate is low volume and low REY content, then this enrichment does not come at the cost of a large reduction in REY recovery. However, it is worth noting that the magnetic concentrate has the highest proportion of critical REY and the lowest proportion of LREY of the processed materials.

Annual production of UK-1 ash is somewhere in the region of 300–350 kt. More importantly, there is at least 16 Mt stockpiled.

Table 3
REY content of various products of processed UK-1 CFA (ppm).

Element	Rougher feed	Rougher concentrate	Magnetic concentrate	Hydrocyclone underflow	Hydrocyclone overflow
La	72.6	54.3	35.7	81.1	90.7
Ce	146.0	108.5	74.3	159.5	177.5
Pr	17.1	13.5	8.8	18.9	21.6
Nd	65.7	52.3	33.9	76.2	83.3
Sm	13.0	11.7	7.4	15.3	17.0
Eu	2.7	2.6	1.5	3.6	4.0
Gd	13.5	10.9	7.3	14.7	17.5
Tb	1.8	1.5	1.1	2.0	2.3
Dy	11.2	9.8	6.4	11.8	15.1
Y	61.1	52.5	37.7	66.1	80.6
Ho	2.1	1.7	1.3	2.2	2.7
Er	5.6	5.0	3.8	6.5	7.9
Tm	0.9	0.8	0.6	1.0	1.1
Yb	5.2	4.5	3.4	5.8	6.9
Lu	0.7	0.6	0.4	0.8	0.9
Σ REY	419	330	224	465	529
LREY (%)	75.0	72.8	71.6	75.4	73.7
MREY (%)	21.5	23.4	24.1	21.1	22.6
HREY (%)	3.5	3.8	4.3	3.5	3.7
Critical	148	124	84	166	193
Uncritical	116	90	59	130	147
Excessive	155	116	80	169	189
Outlook	0.96	1.07	1.05	0.98	1.02
Critical (%)	35.3	37.5	37.7	35.7	36.5
Σ REO	505	398	270	560	637
LOI @ 950 °C	14.2	50.8	na	1.3	1.2

Applying a REO content of 500 ppm to this represents a potential resource of 8000 t. At 2012 US prices, this potential resource would have a value of \$136 M (mischmetal price [26]) although it should be noted that REY prices are volatile and have recently reduced. For 2030, it has been projected that emerging technologies will themselves result in global REO demand of 27,900 t [1]. Clearly, if extraction is technically and economically feasible, this resource is not insignificant. It is important to note that the foregoing relies on the assumption that the entire stockpile contains a similar level of REY. The latter is unlikely to be the case given that REY content varies in both the coal seam and its position in the seam [18].

The technical feasibility of extraction is the next critical parameter that must be investigated to assess the viability of any process. It has been claimed that many REY ores that are found in coal basins are characterised by carbonate and ion-exchangeable modes of occurrence [2]. If this is the case, then extraction processes may be devised that are similar in nature to those developed for the weathered crust elution-deposited ore deposits which typically have a low REY content (0.03–0.25%) and small reserves (3–12 kt) [2]. The weathered crust deposits are viable because of the ease of the extraction. In many ways, a CFA stockpile is analogous to these reserves if they have a similar ease of extraction. The results of this study make it clear that an investigation into the extraction process of UK-1 CFA is necessary. It also lends further support to the idea that other CFAs should be analysed for REY content; it is possible that there are other CFA stockpiles that might contain even higher levels.

4. Conclusion

The current study has highlighted the potential for CFA stockpiles to contain significant REY reserves. It confirms the finding of Hower et al. [19] that REY content in size classified CFA increases as the particle size of the sieved fraction decreases. For the first time, CFA products at various points in a pilot scale processing plant have been analysed for REY content. The results suggest that both fine and coarse IFA can be considered potential REY reserves of UK-1 ash. Extraction of the REY should now be studied to examine the technical feasibility of such a process.

Acknowledgements

The authors would like to thank the Engineering and Physical Sciences Research Council of the United Kingdom, RockTron International Ltd., and the Royal Commission for the Exhibition of 1851. The authors would also like to thank Dr. James Hower and the other anonymous reviewer for their helpful and constructive comments regarding this communication.

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